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Over 1.0 mm-long boron nitride nanotubes

Hua Chen [a], Ying Chen [a,*], Yun Liu [b], Lan Fu [a], Cheng Huang [c], David Llewellyn [a]

[a] Research School of Physical Sciences and Engineering, The Australian National University, Mills Road, Canberra, ACT 0200, Australia
[b] Research School of Chemistry, The Australian National University, Canberra, ACT 0200, Australia
[c] The Electron Microscopy Unit, The Australian National University, Canberra, ACT 0200, Australia

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ABSTRACT

Over 1.0 mm boron nitride nanotubes (BNNTs) were successfully synthesized by an optimized ball milling and annealing method. The annealing temperature of 1100 °C is crucial for the growth of the long BNNTs because at this temperature there is a fast nitrogen dissolution rate in Fe and the B/N ratio in Fe is 1. Such long BNNTs enable a reliable single tube configuration for electrical property characterization and consequently the average resistivity of the long BNNTs is determined to be $7.1 \pm 0.9 \times 10^4\ \Omega$ cm. Therefore, these BNNTs are promising insulators for three dimensional microelectromechanical system.

1. Introduction

Very long carbon nanotubes (CNTs) of over 4 cm have been synthesized [1]. The long nanotubes have many new applications which are impossible for short nanotubes. For instance, long CNTs can be spun into meter-long fibers that are more than an order of magnitude stronger than any current structural materials due to the high Young's modulus [2]. Long metallic nanotubes could be readily assembled into a microelectromechanical systems (MEMS) or nanosemiconductor devices [1]. Boron nitride nanotubes (BNNTs) have the similar nanostructure and about same high Young's modulus as CNTs [3], but they are a wide band-gap semiconductor with the electrical behavior like insulator. So long BNNTs are probably favorable for reinforced composite materials, and might be a complementary of CNTs as an insulator for building up 3D MEMS. In general, BNNTs are more difficult to be synthesized because of the B–N binary system and the involved chemical reactions [4,5]. In this Letter, we report the growth of over 1.0 mm-long BNNTs through an optimized ball milling and annealing process. The electrical resistivity of a single long BNNT is also determined.

2. Experimental

BNNTs were synthesized by an optimized ball milling (Pulverisette 5) and annealing process [4]. In this procedure, amorphous boron powder was first loaded into a stainless steel mill with steel balls (Φ25.4 mm AISI 420) under NH_3 atmosphere of 300 kPa for ball milling treatment at rotation speed of 300 rpm for 50 h. The weight ratio of ball to boron is 50:1. Iron particles were produced and mixed with boron powder in the milling process, and the content of iron particles was about 1.5 at%. The milled powder was then annealed at 1100 °C in a quartz tube furnace in a N_2 flow of 100 ml/min. After 15 h of annealing, a large percentage of powder was transformed into long BNNTs. The structure of BNNT samples was characterized using X-ray powder diffractometer (XRD) (Philips 3020, Co target, 40kV, 30 mA). Scanning electron microscopy (FESEM, Hitachi 4500) was used to characterize the morphology of the samples. Transmission electron microscopy (TEM, Philips CM300) was employed to examine individual structures. Thermal gravimetric analyser (TGA) (Shimadzu TGA-50, N_2, 20 °C/min) was used to monitor nitriding reactions. The conductance of a single BNNT was measured using the two-point configuration. A single nanotube was affixed on Ni electrodes using silver paste (DuPont) and an ohmic contact was achieved after heating the sample at 400 °C in the air for 10 min. *I–V* characteristics of nanotubes were then measured utilizing a pA meter/DC voltage source (HP 4140B).

3. Results and discussion

Fig. 1a is a FESEM image of high-yield, as-synthesized BNNTs with the diameters in the range from 50 to 200 nm. Because the nanotubes are very long, they interwove together. In order to measure the length of individual nanotubes, one single long nanotube was pulled out from the nanotube layer using a sharp wood stick under a stereoscopic microscope. The nanotube was placed on the surface of a silicon substrate and the length was measured under FESEM. One of long nanotubes is shown in Fig. 1c and its length is over 1.0 mm. The original length of this tube may be even longer as the nanotube could be broken during the pulling. To our best knowledge, these nanotubes are the longest BNNTs synthesized so far. The TEM image in Fig. 1b, clearly reveals bamboo characteristic structure. The tip Fe particle acts as responsible catalyst [6,7]. These results were confirmed by XRD analysis. The XRD pattern

* Corresponding author. Fax: +61 2 61250511.
E-mail address: ying.chen@anu.edu.au (Y. Chen).

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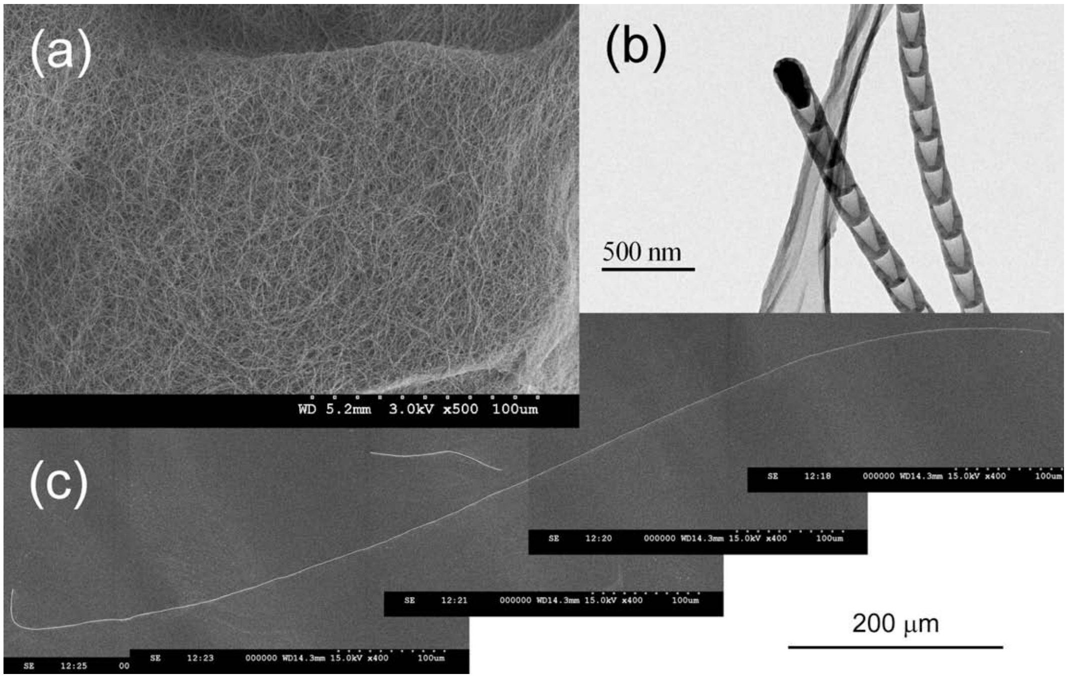

Fig. 1. (a) FESEM image of high-yield as-synthesized BNNTs, (b) TEM image revealing a bamboo-type structure and (c) FESEM image showing a single over 1.0 mm-long BNNT.

illustrated in Fig. 2 shows the diffraction peaks associated to h-BN, α-Fe and γ-Fe phases. The broad h-BN (002) peak is due to the small size effect of BNNTs. The Fe peaks are consistent with the catalytic Fe particles detected under TEM.

The formation of such long BNNTs of special bamboo structure suggests interesting growth mechanisms. The long BNNTs were synthesized using an optimized ball milling and annealing process [4], in which boron powder was first ball milled in NH_3 atmosphere at room temperature and followed by annealing in N_2 gas of 100 ml/min at 1100 °C for 15 h. This long annealing or growth time suggests a very slow growth process for the long BNNTs. In the case of ultra long carbon nanotubes, a much shorter growth time of 1 h was required for the 4 cm CNTs [1]. The growth rate of the long BNNTs at 1100 °C was estimated by measuring three longest nanotubes from each sample obtained after different growth times (1, 2, 4 and 15 h), the corresponding length is 0.13, 0.31, 0.50 and 1.05 mm, respectively. At the beginning stage (first 4 h), the growth rate is about 34.7 nm/s and it is lower during further growth up to 15 h. This raises the questions of what the critical parameters controlling the growth of long BN nanotubes are. In the current case, the nanotubes grow out from the milled boron sample during the annealing process, in which nitriding reaction is needed first to convert B to BN prior to form BN nanotubes [8]. The special bamboo-type structure suggests that the long nanotubes are formed via metal catalytic growth mechanism which has been extensively investigated [9–14]. In metal catalyst growth process, during the annealing process, B atoms diffuse into a Fe particle while the N_2 is decomposed to the N atoms on the surface of Fe particle and also diffuse into it. When the BN species are supersaturated (the austenite iron can only accommodate a very limited boron (~0.06 at%) [15] within the annealing temperature range), they precipitate layer by layer to form the BNNTs.

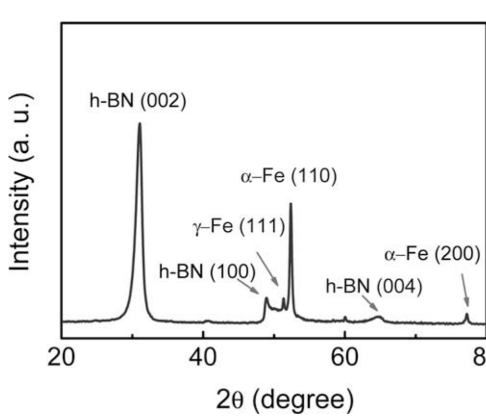

Fig. 2. X-ray powder diffraction pattern for BNNTs.

Fig. 1a also shows high-purity BNNTs produced via the above catalytic process and no BN particles can be found, which suggests that the nitriding reaction process at 1100 °C corresponds to the dissolution and precipitation process of B and N through Fe particle because direct reaction between B and N_2 normally requires a much high temperature [16]. The nitriding reaction of the ball milled B (15.20 mg) was investigated using TGA analysis. The sample weight changes as a function of temperature are shown in Fig. 3. The weight increases as the temperature increasing due to the absorption of N_2, dissolution of N in Fe and BN formation. The peak in the differential curve around 1050 °C indicates a fastest reaction rate. Isothermal annealing over this temperature range will maintain the fast formation of BN phase, which is an important factor for growing long nanotubes.

Because the annealing temperature around 1100 °C is below the melting point of the stainless steel (>1300 °C), Fe catalyst particles were not in liquid state but could be in a quasi-liquid state because of nanometer-scaled size [17,18]. Based on the B–Fe–N phase diagrams at 950 °C, 1050 °C and 1150 °C [15], the ratio of B and N (B/N) dissolved in the Fe increases dramatically with the increasing temperature and is close to 1 when the temperature is at about 1130 °C. If the temperature is too high (i.e. 1300 °C), nanosized catalyst particles would be melted and merged together to become large particles to impede the growth of bamboo BNNTs, and also the boron particles would react directly with nitrogen to form BN particles and used up the boron source [19]; if the temperature

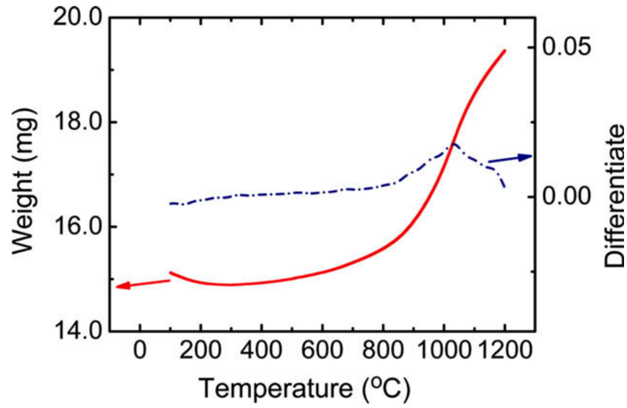

Fig. 3. TGA and associated differential curves, presenting the weight increase as a function of temperature.

is too low (i.e. 900 °C), the low diffusion rate of the B and N in iron would slow down the precipitation rate of BN layers (growth rate of BNNTs), which are consistent with the TGA results. Therefore, the selected annealing condition (1100 °C) provides two possible controlling parameters for the formation of the very long BNNTs: faster N dissolution rate in Fe and the B/N ratio (about 1) in Fe. Both factors ensure a highest formation rate of BN phase. However, at 1100 °C, the TGA analysis shows a very high weight increase rate of 9.8×10^{-3} mg/s, which corresponds to the fast growth rate of nanotube at the beginning of the growth, but the observed low growth rate during further growth period indicates that the growth process of the long nanotubes is certainly not limited to the reaction rate but might be related to the slow precipitation rate of BN layers into the formation of the special bamboo structure. Note the fact that the diameter distribution of the BNNTs almost remains unchanged in comparison with the longitudinal growth of BNNTs during annealing, the growth process of the long BN nanotubes is most likely limited by the slow formation of BN layers at the interfaces between the catalyst and BN shells. With the increasing the curvature of BN layers, the catalyst particle is sucked into the nanotube by the capillary effect [10,20], which leads to the decreasing in the contact area of iron and boron powder. The bamboo BNNTs grow longer through repeating the above processes, which possibly is responsible for a very long growth time.

The successful synthesis of the very long BNNTs makes it possible to accurately measure their physical properties since a single long tube can be manipulated under an optical microscope. Being a wide band-gap semiconductor, h-BN has a very high resistivity (the resistivity of h-BN thin films is in the range of 10^{11}–10^{14} Ω cm and the bulk h-BN's receptivity is at the order of 10^{14} Ω cm). In contrast, the reported resistivity of the BNNTs is far away from the above value (300 Ω cm for pure single BNNT and 0.2–0.6 Ω cm for fluorine-doped single BNNT) [21]. The big difference between them needs to be clarified. The conventional four-probe setup or two-probe method on the Si wafer can work well on measurement of electrical properties of CNTs [22] or fluorine-doped BNNT [21], but it is not suitable for insulating BNNTs, because the huge insulation between electrodes should be considered (for example the electrodes are too close to each other and insulator layer SiO_2 on the surface of Si wafer is too thin). These factors may induce a compatible background resistance. The electrical resistivity of a single long BNNT has been measured using a measurement setup shown in Fig. 4. Two Ni electrodes are installed onto an alumina ceramic plate with a gap of 10 mm for a good insulation and their tips are bent close to each other, which greatly avoids the influence of the resistance from the holder, leading to a reliable measurement. A single BNNT is fixed between the two tips of electrodes by conductive silver paste (DuPont). The electrical contact is further improved by heating the system at 400 °C in the air for 10 min, ensuring an ohmic contact between the BNNT and Ni electrodes [23]. The length of the tube between two electrodes is about 47 μm and the diameter is around 157 nm. These data will be used for calculating the resistivity of the single BNNT later.

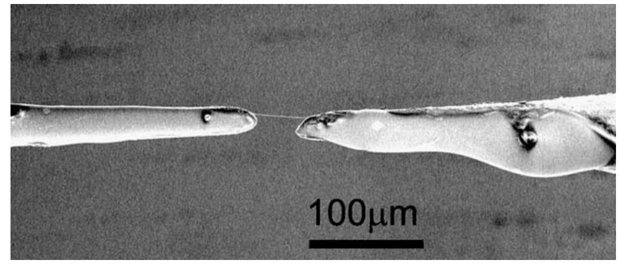

Fig. 4. FESEM image of a single BNNT connected on a pair of Ni electrodes.

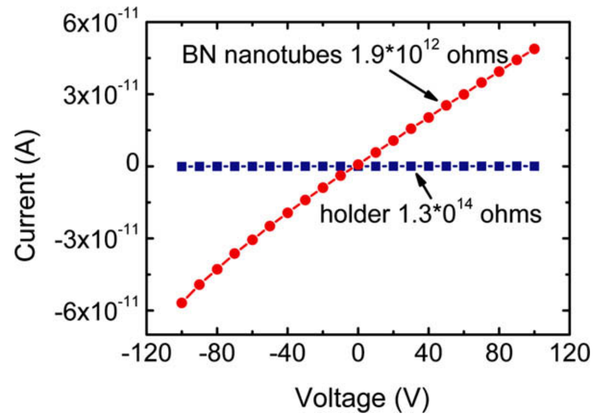

Fig. 5. The *I–V* curves of the sample holder and of a single BNNT.

The *I–V* characteristic of the single BNNT (see in Fig. 5) was investigated using a pA meter/DC voltage source (HP 4140B). The *I–V* curve without BNNT (i.e. open circuit or background signal from the sample holder) was also measured for the purpose of comparison. The resistance of the single BNNT is 1.9×10^{12} Ω, corresponding to the electrical resistivity of 7.8×10^4 Ω cm. The resistance of the holder without sample is 1.3×10^{14} Ω. The *I–V* curve of the BNNT is linear confirming an ohmic contact between the BN and electrodes. The average value of the measured resistivity from eight individually BNNTs was $(7.1 \pm 0.9) \times 10^4$ Ω cm. The resultant value of the BNNT's resistivity is much higher than the previous report [21].

4. Conclusions

BNNTs with the length over 1.0 mm have been successfully synthesized by an optimized ball milling and annealing method. The annealing temperature of 1100 °C is crucial for long BNNTs growth because there is a faster N dissolution rate in Fe and the B/N in Fe is close to 1, which ensures the high nitriding reaction. Benefiting from such long BNNTs, the reliable single tube configuration has been set up for measuring electrical property. The average resistivity of the long bamboo BNNTs is $7.1 \pm 0.9 \times 10^4$ Ω cm.

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